Frustrated Itinerant Magnetism

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frustrated magnetic systems are those where there are topological restraints such that all magnetic interactions cannot be satisfied simultaneously. This concept was initially applied to local moment systems; relatively recently it has been realized that in itinerant systems where atoms are close to the magnetic instability condition, frustration can be at the origin of exotic magnetic structures and striking effects in the paramagnetic state. The models and experimental data on these systems will be briefly reviewed.

I. Local moment systems

The word "frustration" was introduced in the context of magnetic systems by Toulouse[1] to express the type of situation where magnetic interactions cannot all be satisfied simultaneously, so that the ground state is necessarily a compromise. Initially this concept was applied to "classical" model systems where the moment at each site is fixed in magnitude but not in direction. Thus for the one dimensional Ising system of figure (1a), if the near neighbour interaction J_1 is either ferromagnetic or antiferromagnetic while the next nearest neighbour interaction J_2 is antiferromagnetic, the two types of interaction cannot be satisfied simultaneously. In general for near neighbour interactions topological frustration occurs when in a lattice the number of antiferromagnetig interactions in a plaquette is odd. This happens for triangular lattices with antiferromagnetic interactions, or for square lattices if the interactions are chosen appropriately (figures 1b and 1c). In addition to regularly frustrated lattices where there is frustration but no disorder among the set of interactions, there are also random systems (spin glasses) where the set of interactions is chosen at random in such a way that there is topological disorder among the interactions as well as (partial) frustration. Thus in the square lattice if each interaction is chosen with random sign, exactly half the plaquettes are frustrated and these frustrated plaquettes are distributed in a random manner.

There are many physical examples of regularly frustrated and randomly frustrated local moment systems, particularly in intermetallic compounds and in alloys where the existence of long range RKKY-like interactions enhances the probability of frustration. Regular rare earth intermetallic compounds with frustrated interactions can show a wide range of complex magnetic phases: anti-phase structures ($DyNi_2Si_2$, $TbFeSi_2$), modulated phases ($PrNi_2Si_2$), helimagnetism (Tb, Dy, Ho) or non-collinear structures (DyNi, Er Ni)[2]. Some compounds show numerous quasi-degenerate phases which are either commensurate or incommensurate with a "devil's staircase" phase structure as a function of temperature and field . Recently considerable attention has been paid to Kagomé lattices ($SrCr_{8-x}Ga_{4+x}O_{19}$ and pyroclore) which are made up of triangular units assembled around hexagons[3]. They are quasi two dimensional and uniformly frustrated; despite their having strong near neighbour interactions they seem to show no long range order at any temperature.

The theory of frustrated local moment systems has been studied extensively, starting from the antiferromagnetic triangular Ising system[4]. The major characteristic of frustration is the possibility of having many degenerate ground states. The frustrated system, with or without topological disorder, can be stabilized in degenerate spin configurations which are not related to each other by a global symmetry (inversion on the case of Ising spins or global rotation for Heisenberg spins). A well studied example for classical spins is the 3d ANNNI (Anisotropic Next Nearest Neighbour

Ising) model. This model assumes Ising spins on a cubic lattice with ferromagnetic interactions J_0 in the planes, and competing near neighbour J_1 and second neighbour J_2 interactions along the z directions[5]. Tliis model shows a rich field of phases where different stacking sequences are stable. A qualitatively similar phase diagram with a succession of commensurate and incommensurate phases is observed in rare earth compounds such as $DyGa_2$ under applied field[6].

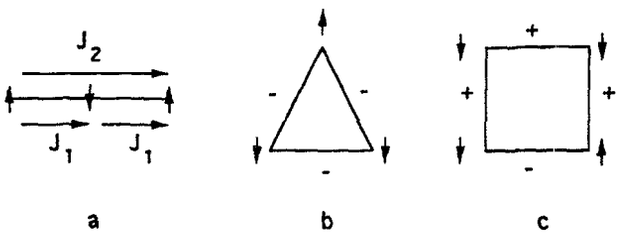

Figure 1. a. Frustration due to competing interactions in a one dimensional ANNNI model. If the second neighbour interaction is antiferromagnetic, wliatever the sign of tlie nearest neighbour interaction the system will be frustrated. b. Topological frustration for Ising spins in a triangle witli antiferromagnetic interactions. There is no way in wliich all tlie three interactions can be satisfied. c. Topological frustration for Ising spins in a square witli three ferromagnetic interactions and one antiferromagnetic interaction of the same strengtli. One of the interactions must always be frustrated and there are eight alternative lowest energy states.

At finite temperatures, not too far below tlie temperature where the magnetic order first sets in, in the presence of long range interactions tlie magnetic phase will tend to be that with a vector of propagation Q such that the transform of the interactions $J(q)$ is maximized. In these modulated or helimagnetic structures different spins have different time average magnetic moments; a famous example is Cr metal which has a modulated antiferromagnetic order. As the temperature is lowered these structures will in general square up and go over to antiphase structures where all spins have their maximum moment[2].

II. Model Itinerant systems

Up to now we have considered only classical spins whose moments are fixed in amplitude. In itinerant magnetic systems however the local moment is not fixed but depends to a great extent on tlie molecular fields exerted on it by its neighbours as well as on parameters such as tlie external field and the pressure. Thus in tlie canonical Stoner model of ferromagnetism, a metal with a sufficiently high density of states at the Fermi level becomes ferromagnetic at low temperatures by a bootstrap mechanism where each site acquires a moment aided by the interactions with the moments on the neighbour sites. Weak ferromagnets and their excitations (as in $ZrZn_2$ for instance) are well described by this model,

If interactions are topologically frustrated, one can imagine a situation where on the contrary a ground state can exist where neighbour sites conspire to resolve the frustration by annuling the moment on certain sites. Thus if the correlation energy at a site U is weaker than tlie intersite interaction strength J, then for a triangle of frustrated spins with antiferromagnetic interactions (figure 2) it will be energetically favourable to suppress the moment on one of the three sites, fig. 2b, ratlier than maintaining the frustration of fig. 2a. (inost "crimes passionnels" follow this patten).

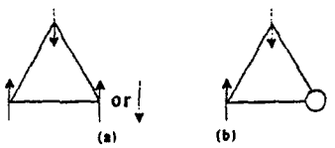

Figure 2. a. A frustrated triangle of Ising spins with antiferromagnetic interactions. b. The same triangle where one of the spins has had *its* moment supressed.

A very instructive theoretical model has been developed[7] which expresses this idea starting from a Hubbard Hamiltonian for spins on a two dimensional triangular lattice. It is assumed that the on-site Coulomb repulsion U is of the order of the bandwidth W and that the system is close to the magnetic-nonmagnetic instability. In addition the spin sites are assumed to be very anisotropic so that each spin can take the values up, down or zero. The effective spin 1 Hamiltonian can then be written

$$\Delta \sum_i (S_i^2) + 1/2 \sum_{i \neq j} (J_{ij} S_i S_j)$$

where A and J_{ij} are related to the parameters of the Hubbard model. Now if A is positive the S_i can take the three values: ± 1 with a magnetic moment on the site, or 0 when tlie site is nonmagnetic which is the ground state in the absence of exchange or an external magnetic field. For tlie model to exhibit the principal efects, it is

suficient to restrict the interactions to a near neighbour interaction J_1 and a second neighbour interaction J_2. At zero temperature tlie phase diagram as a function of the ratios Δ/J_1 and J_2/J_1 shows four phases; as well a as a nonmagnetic phase and two antiferromagnetic phases where all tlie spins have ± 1 moments there is a phase with both magnetic and nonmagnetic sites. As Δ is positive, forming a magnetic moment costs energy and for certain parts of the phase diagram it is energetically favourable to have zero moment sites. (It can be checked that the total molecular field on the zero moment sites is zero).

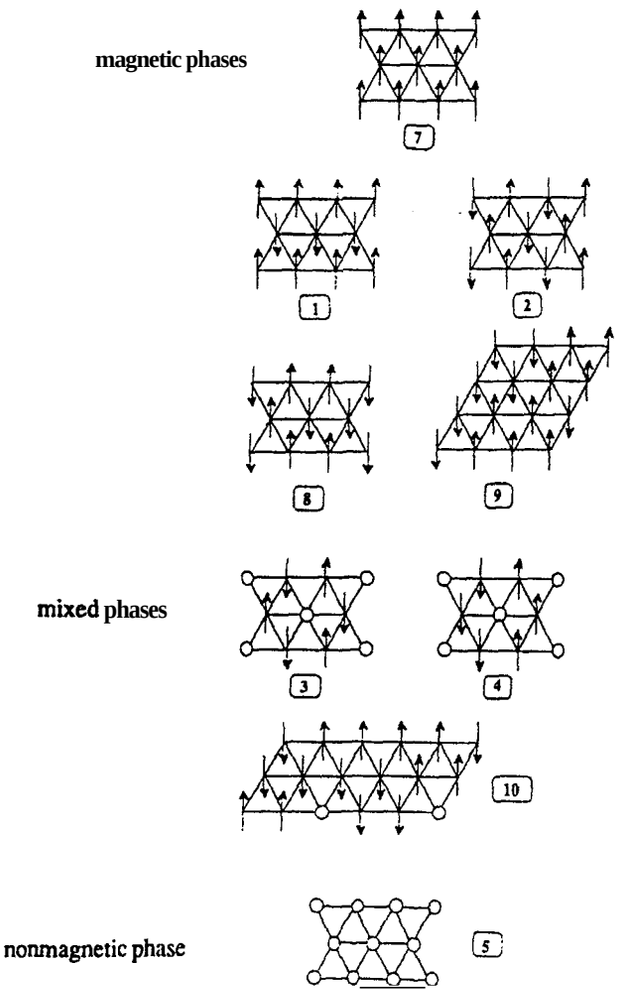

Figure 3a. Tlie possible zero field states for tlie spin 1 two dimensional triangular model. o indicates a nonmagnetic site.

If now a magnetic field is applied, a furtlier rich sequence of phases can appear. Thus for the particular case $A = J_1$ and $J_2 = J_1/2$ (antiferromagnetic ground state III in figure 3) the magnetization increases as shown in figure 4 with a phase sequence as a function of applied field which includes two phases with zero moment sites. Both in zero field and in field it can be energetically favourable for certain sites to have zero moment, a "mixed" structure.

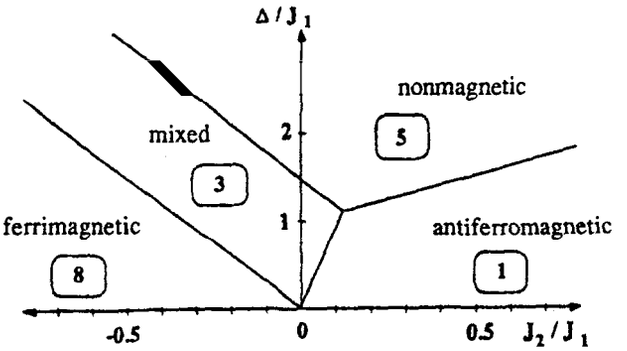

Figure 3b. Tlie zero field phase diagram as a function of tlie ratios Δ/J_1 and J_2/J_1. (reference 7)

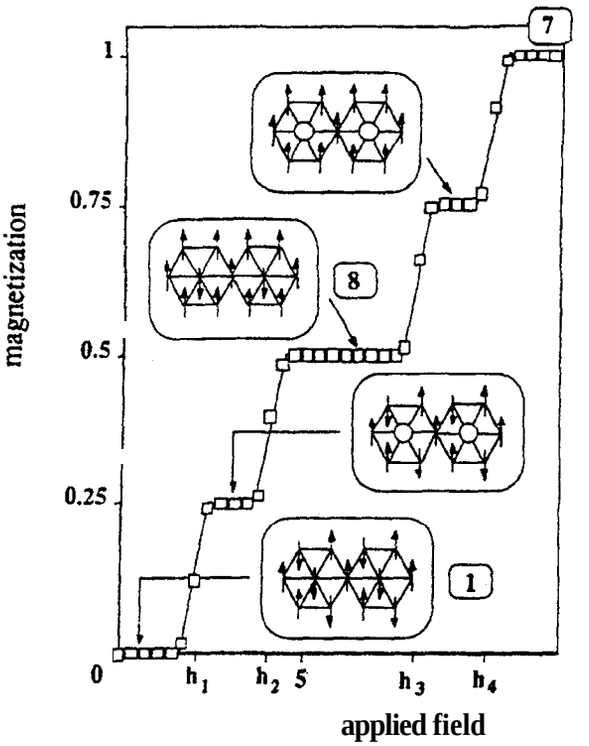

Figure 4. Tlie phase diagram as a function of field for tlie spin 1 two dimensional triangular model with the particular choice of parameters $\Delta/J_1 = 1$ and $J_2/J_1 = 0.5$. The applied field is in units of Jl and the magnetization is relative to tlie fully magnetized state. (reference 7)

It can be shown that if we have the same Hamiltonian but with classical spins (all orientations permitted) there will never be zero moment sites in the ground

state; the frustration will be sufficiently reduced by a collaborative canting of the spins, figure 5. It is thus essential to have strong anisotropy for zero moment sites to appear in this model. The effect of anisotropy has been discussed in a quantitative Hubbard model[8], where phase diagrams are given including antiphase and mixed phases as in the discussion above, but also helicoidal and sine wave phases. The form of the phase diagram depends on the relative strengths of the correlation energy Δ, the anisotropy D, the couplings and the magnetic field. Mixed structures appear for finite D or field and one can estimate what dose of anisotropy is necessary for a mixed structure to appear. Alternatively even with zero anisotropy if the structure can deform (exchange magnetostriction), a mixed structure can be stabilized by distortion. Finally we can note that magnetic sites always have larger volumes than non-magnetic sites so mixed structures will be associated with a diminution in volume.

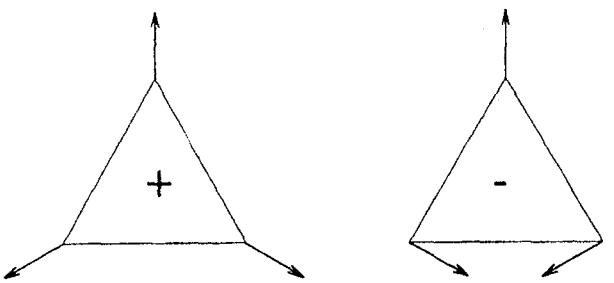

Figure 5. Two possible lowest energy state configurations for a frustrated triangle of XY spins.

III. $REMn_2$ structures

The discussion given above may seem over simplified but it turns out that it provides a remarkably cogent explanation of the exotic magnetic structures observed experimentally in the intermetallic compounds $REMn_2$.

There are three main families of RE-Mn intermetallic compounds: $REMn_{12}$, RE_6Mn_{23} and $REMn_2$. In all of these the Mn-Mn interactions are antiferromagnetic and the structures are such that two nearest neighbours can be nearest neighbours of each other as in a triangular structure or a tetrahedron, so the conditions for frustration are fulfilled. The $REMn_2$ series is particularly interesting as in addition the Mn moments are close to the conditions for instability of band magnetism. The compounds form in the hexagonal C14 or F.C.C. C15 Laves phases; in both structures Mn atoms are at the summits of regular tetrahedra, which form chains in the hexagonal case and a diamond superstructure in the cubic case. Indirect evidence shows clearly that the the Mn sites in these compounds are strongly anisotropic with in plane moments favoured[9]. The Mn-Mn interactions are an order of magnitude stronger than the RE-Mn or RE-RE interactions so to a first approximation only the former need be considered. There are large magnetovolume anomalies in this series which is the characteristic signature of band moment instability[10]. As a quite general rule in band magnetism, if a site is magnetic it occupies a larger volume than if it is not magnetic; this is the mechanism which gives rise to the invar effect in FeNi alloys, and in the CuMn alloy series at the dilute Mn end where the Mn atoms are strongly magnetic the effective volume occupied by each Mn atom is much larger than near the pure Mn end where the magnetic moments are small. In the $REMn_2$ family it turns out that there is a critical Mn-Mn distance (d_c = 2.66A); when the Mn-Mn separation is lower than d_c as in $ScMn_2$, $ErMn_2$, and $HoMn_2$, the Mn is nonmagnetic and only RE magnetism survives, while for the Mn-Mn distance larger than d_c ($PrMn_2$, $NdMn_2$, $GdMn_2$, and $SmMn_2$) the Mn moments are large (about $2.7\mu_B$) in the ordered state. A fairly large increase in volume takes place at the magnetic ordering transition, indicating that in the paramagnetic state the fluctuating local moments on the Mn sites are lower than in the ordered state. The most striking effects are seen for the two compounds YMn_2 and $TbMn_2$, where the Mn-Mn distance is close to the critical value. There are giant increases in volume on ordering (a few percent volume change) with strong hysteretic effects on temperature cycling[10]. Chemical pressure can modify the magnetic ordering considerably in these marginal cases; thus the replacement of a small fraction of Y by Sc which shrinks the lattice eliminates the magnetic order; inversely the introduction of La expands the lattice and stabilizes the magnetism[11]. To summarize, this family of compounds thus unite all the different conditions specific to the model outlined above: frustrated interactions, strong anisotropy, itinerant magnetism with magnetic instability. In remarkable confirmation of the model it is precisely in these compounds that "mixed" magnetic structures with coexisting magnetic and nonmagnetic sites are observed.

In $DyMn_2$ in zero applied field there is a mixecl structure wliere only 25% of the chemically equivalent Mn sites have magnetic moments, the rest having zero moments[12]. In $TbMn_2$ the magnetic structure in zero field is complex with all the Mn atoms in a magnetic state, but there is a transition to the same "mixed" structure when a magnetic field of 4.5T is applied at 25K or when a few percent of Mn atoms are replacecl by smaller Fe atoms[13]. In $ThMn_2$ which is also close to the critica1 condition the Mn atoms order in a triangular antiferromagnetic mixed structure[14]. In other compounds of tlie same family, even if the striicture is not mixed tlie influence of the frustration is very important; in tlie ordered structures the frustration is resolved with collinear or complex propagation vectors ($PrMn_2$, $NdMn_2$[9]) or with a distorted helicoidal modulation (YMn_2[9]). Similar structures can be induced by hydrostatic or chemical pressure[15] in certain other compounds. As one might expect, in all these systems the effects of hydrostatic pressure are dramatic and small changes in pressure acting upon the lattice parameters give huge changes in ordering temperatures[16].

Frustration continues to play an important role in the paramagnetic state where giant spin fluctuations appear. In particular the compound YMn_2 has been intensively studied[17]. The ground state is a helically modiilated antiferromagnet witli a long period of 400Å and two modulation modes[9]. If pressure is applied or the lattice is doped witli Sc in the place of Y to provide chernical pressure, the ordering is suppressed[18] and the system becomes heavy fermion like witli a large electronic specific heat and electron-electron resistivity term[19]. YMn_2 substituted with **3%** Sc is paramagnetic down to zero teinperature; the electronic specific heat coefficient is 140 mJ/K^2 which is a value quite comparable with the heavy fermion systems. The giant antiferromagnetic spin fluctuations in the paramagnetic state lead to strongly enhanced paramagnetic neutron scattering about tlie antiferromagnetic wavevector for a wide range of temperature. The effective local moment on the Mn sites increases strongly with increasing temperature, tending towards the full Mn magnetic moment at very high temperatures. Thus from integration of neutron scattering intensity, in YMn_2 the effective fluctuating local moment increases from about 1 μ_B at 90K, the ordering teinperature, to about 2 μ_B at 300K[17]. The transport properties in the paramagnetic state reflect the anomalous magnetic behaviour.

If a fraction of Mn atoms are now replaced by Al atoms the quantum spin liquid state transforms to a spin glass state because of local lifting of total frustiation which allows static local moments to form[11]. The system closely follows the qualitative behaviour predicted in a model of a fully frustrated lattice with dilution[11]. The formation of a spin glass is accompanied by other changes in physical parameters.

IV. Other transition **metal** systems

Althougli the $REMn_2$ compounds have been the most intensively studied, there are certainly other systems where frustration produces analagous effects on transition metal sites which are close to the condition for instability. In the Laves phase compound $TiFe_2$, tlie ordered state is antiferromagnetic with 1/3 of the Fe sites which are nonmagnetic[20]. In field neutron nieasurements indicate that these Fe sites are not paramagnetic but have zero moments in the same sense as in the $REMn_2$ compounds. In the compound $Mn\,Si_3$ whicli has a very complex magnetic structure the neutron data indicate that there are Mn sites which have zero moments in the ordered state[21]. For both of these compounds frustration can be invoked.

Pure Mn metal has three different structures α, β and γ; β is nonmagnetic, y is antiferromagnetic with all sites carrying the same moment of about $2\mu_B$ and a is a complicated noncollinear antiferromagnet with some sites having moments up to $1.8\mu_B$ and some close to zero[22]. It is possible that this structure may be the consequence of frustration.

Another element which frequently shows moment instabilities is U. In the compound UNi_4B[23] a mixed structure has been shown to exist.

The only systems we have discussed are those with regular atomic structures. It may be possible to extend the ideas to disordered systems. For instance there are spin glass alloys where the local moments are close to the instability condition; in such alloys the local moments may well be not only disordered in the sense that the moment orientations are quasi-random, but there may be associated variations in the moment am-

plitudes. CrFe alloys may provide an example of this type of behaviour.

V. Instable rare earth moments: CeSb

We have seen that effects specific to itinerant inagnetic systems under tlie influence of frustration appear most clearly in situations where tlie local magnetic moments are instable. As well as the 3d magnets, one can also search for such effects in rare eartli compounds containing Ce or Yb. Tlie typically "heavy fermion" compounds show unstable local moments and indeed certain compounds have characteristics which closely resemble those of tlie compounds that we have discussed above. A particularly clear example is the semi metal CeSb. This has one of the most complex magnetic phase diagrams ever discovered[24]. It crystallizes in a single NaCl structure with a very small crystal field splitting and a very large cube edge inagnetic anisotropy. The properties are very sensitive to hydrostatic pressure and to tlie applied field. In zero field there is a succession of six modulated commensurate phases with different stackings of ferromagnetic planes with up or down magnetization and of nonmagnetic planes; more mixed phases appear in an applied field[25]. As all tlie planes perpendicular to the modulation direction have an interna1 ferroinagnetic (or zero moment) order, and tlie moment are "squared up", i.e. tlie moments in all the ferromagnetic layers are equal, tlie structures can be very conveniently represented by one diinensional figures. Some of the structures are sliown in figure 6. The sensitivity of tlie Ce moment to the various parameters implies a delicate balance between tlie f-p liybridisation, tlie crystal field and the frustrated interactions[26]. CeSb is a member of the family of Kondo lattices so the sites at whicli the Ce moments are zero can be considered either as "nonmagnetic" or "Kondo". Tlie excitation spectra seem to suggest that the nomagnetic layers are not zero moment in tlie sense of the compounds discussed above, but paramagnetic, meaning that they have rapidly relaxing local moments rather than moments which are supressed by tlie band structure effects. Tlie ANNNI model[5], which may be thought of as a one dimensional moclel with frustration because of competing nearest neighbour and second neighbour interactions, can provide an excellent framework for understanding the complexity of tlie magnetic structures and the succession of modulated phases. As in its original version it is an Ising model (each spin either up or down) it cannot provide an interpretation for the zero moment planes in the mixed structures in the same way as the effective spin 1 model outlined above.

ferro	+ + + + + + + + + + + +
ferro mixed 1	+ + + o + + + o + + + o
ferro mixed 2	+ + o o + + o o + + o o
ferro mixed 3	+ + o o + + o o + +
ferro mixed 4	+ + + o o + + o o + + + o o
ferro mixed 5	+ + + o o + + + o o + + +
ferri 1	+ + - - + + - + + - - + +
fem 2	+ + - + + - + + - + +
antiferro mixed 1	+ o - + o - + o -
antiferro rnixed 2	- + + - o + - - + o - + o -
antiferro mixed 3	- + + - - + o - + + - - + o
antiferro rnixed 4	+ - - + + - - + o +
antiferro mixed 5	+ + - - + + - - + o - + + - -
antiferro 1	+ - + -
antiferro 2	+ + - - + -
antiferro 3	+ + - - + - - + + -
antiferro 4	+ + - -

Figure 6. Tlie modulated magnetic phases of CeSb. Tlie structiire is a siiccession of ferromagnetic or zero moment (001) planes with the magnetic moments along the modulation c axis and so perpendicular to the planes. Up or down magnetization planes are indicated + or -; zero moment planes are indicated o. (reference 25)

VI. Conclusion

Frustration in itinerant systems has a dramatic effect on the magnetic ordering and can produce zero moment sites in tlie ordered state when the systems are close to the condition for magnetic instability. In the paramagnetic state effects which mimic heavy fermion behaviour appear and the effective local moments are

highly temperature dependent. There are strong hydrostatic pressure dependences at all temperatures. This novel and striking behaviour has only been interpreted relatively recently and there are certainly many other examples of systems which exhibit itinerant frustration waiting to be discovered. It would be very interesting to pursue the discussion of the relatioiiship between frustratioii and heavy fermion effects.

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References

1. G. Toulouse, Comm. Phys. 2, 115 (1977).
2. D. Gignoux and D. Schmitt, in *Handbook* of *Physics* and *Chemistry* of Rare Earths, edited by K. A. Gschneider and L. Eyring, (Elsevier, Amsterdam 1995) Vol. 20, p 293.
3. J. Villain, Z. Phys. B, 33, 31 (1979); A. P. Ramirez, J. App. Phys., 70, 5952 (1991); E. F. Shender, V. B. Cherepanov, P. C. W. Holdsworth and A. J. Berlinsky, Phys. Rev. Lett., 70, 3812 (1993).
4. R. M. F. Houtappel, Physica 16, 425 (1950); G. Wannier, Phys. Rev. 79, 357 (1950).
5. J. von Boehm and P. Bak, Phys. Rev. Lett. 42, 122 (1979).
6. D. Gignoux, D. Schmitt, A. Takeuchi and F.Y. Zhang, J. Mag. Mag. Mat. 97, 15 (1991).
7. R. Ballou, C. Lacroix and M. D. Nuíiez-Regueiro, Pliys. Rev. Lett. 66, 1910 (1991); R. Ballou, B. Ouladdiaf, P. J. Brown, M. D. Nuñez-Regueiro and C. Lacroix, Phys. Rev. B 45,3158 (1992); C. Pinettes and C. Lacroix, J. Phys. Cond. Mat. **6,** 10093 (1994).
8. M. D. Nuñez-Regueiro and C. Lacroix, Phys. Rev. B 50, 16063 (1994).
9. R. Balloii, J. Déportes, R. Lemaire, Y. Nakamura and B. Ouladdiaf, J. Mag. Mag. Mat. 70, 129 (1987); It. Ballou, J. Déportes, R. Lemaire and B. Ouladdiaf, J. Appl. Phys. 63, 3487 (1988).
10. H. H. Wada, H. Nakamura, K. Yoshimura, M. Shiga and Y. Nakamura, J. Mag. Mag. Mat. 70, 134 (1987).
11. M. Shiga, J. Mag. Mag. Mat. 4; 17 (1994).
12. K. Yoshimura and Y. Nakamura, J. Phys. Soc. Jpn. 53, 3611 (1984); C. Ritter, S. Kilcoyne and R. Cywinski, J. Phys. Cond. Mat. 3, 727 (1991).
13. P. J. Brown, B. Ouladdiaf, R. Ballou, J. Déportes and A.S. Markosyan, J. Phys. Cond. Mat. 4, 1103 (1992).
14. K. H. J. Buschow, Sol. St. Comm. 21, 1031 (1977); J. Déportes, R. Lemaire, B. Ouladdiaf, E. Roudaut and F. Sayetat, J. Mag. Mag. Mat. 70, 191 (1987).
15. M. Shiga, J. Hirokawa, H. Wada and Y. Nakamura, J. Phys. Soc. Jpn. 59, 1410 (1990).
16. J. Voiron, R. Ballou, J. Déportes, R.M. Galera and E. Lelièvre, J. App. Phys. 69, 5678 (1991).
17. M. Shiga, H. Wada, H. Nakamura, K. Yoshimura and Y. Nakamura, J. Phys. F17, 1781 (1987); J. Déportes, B. Ouladdief and K.R.A. Ziebeck J. Mag. Mag. Mat. 70, 14 (1987).
18. H. Nakamura, H. Wada, K. Yoshimura, M. Shiga, Y. Nakamura, J. Sakurai and Y. Komura, J. Phys. F 18, 981 (1988).
19. H. Wada, H. Nakamura, E. Fukami, K. Yoshimura, M. Shiga and Y. Nakamura, J. Mag. Mag. Mat. 70, 17 (1987); R. A. Fisher, R. Ballou, J. P. Emerson, E. Lelièvre-Berna and N. E. Phillips, Int. J. Mod. Phys. B7, 830 (1992).
20. P. J. Brown, J. Déportes and B. Ouladdiaf, J. Phys.Cond. Mat.4, 10015 (1992).
21. P. J. Brown, J. B. Forsyth, V. Nuñez and F. Tasset, J. Phys. Cond. Mat. 4 , 10025 (1992).
22. S. A. M. Mentink, A. Drost and J. A. Mydosh Phys. Rev. Lett. 73, 1031 (1994).
23. T. Yamada, N. Kunitomi, Y. Nakai, D.E. Cox and G. Shirane, J. Phys. Soc. Jpn. 28, 615 (1970).
24. T. Chattopadhyay, Science 264, 226 (1994).
25. H. Bartolin, P. Burlet, S. Quezel, J. Rossat-Mignod and 0. Vogt, J. Physique 40 C5, 130 (1979).
26. H. Takahashi and T. Kasuya, J. Phys. C 18, 2697 (1985).